"Results from the U.S. Great Lakes Fish Monitoring Program and Effects of Lake Processes on Contaminant Concentrations"

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ABSTRACT

An analysis of composites samples of 820 lake trout, walleye, steelhead, Chinook, and coho from the Laurentian Great Lakes reveals differences in contaminant processing among and between lakes which results in differing concentrations of bioaccumulative contaminants. Generally, contaminants are most concentrated in fish from Lake Michigan and least concentrated in fish from Lake Superior, with the notable exceptions of toxaphene and alpha-HCH. Differences in contamination patterns, however, are apparent not only among the lakes but between sites within a lake or even fish within a site. Lake trout composites from Lake Superior show an increase in the degree of chlorination of PCBs with increasing total PCBs. The PCB congener profile of lake trout from the Sturgeon Bay site of Lake Michigan is substantially different from that of the Saugatuck site of Lake Michigan, possibly due to the influence of contamination from nearby Green Bay. Finally, the ratios of selected PBDE and PCB congeners are significantly different in Lake Superior fish compared to fishes from all the other lakes. We hypothesize that this is a result of the colder temperatures and associated lower plankton growth rates in Lake Superior allowing PCB and PBDE uptake by phytoplankton to reach near equilibrium, thus enhancing the relative concentrations, in phytoplankton and the food web in general, of congeners that may be kinetically limited in other lakes.

INTRODUCTION

The Great Lakes Fish Monitoring Program (GLFMP) is administered by the US EPA Great Lakes National Program Office (GLNPO) and is one of the longest running contaminant monitoring programs on record. The program has two components: the first element monitors contaminant concentrations in top predator fish species from each lake. Concentrations are monitored in composites of five whole lake trout (*Salvelinus namaycush*) of standard size in all lakes except Lake Erie, and in walleye (*Stizostedion vitreum vitreum*) in Lake Erie. These data are used to assess time trends in organic contaminants in the open waters of the Great Lakes, using fish as biomonitors. These data can also be used to assess the risks of such contaminants on the health of this important fishery, and on wildlife that consume them. The second element of the GLFMP focuses on assessing human exposures via consumption of popular sport fish, including coho salmon (*Oncorhynchus kisutch*), Chinook salmon (*Oncorhynchus tshawytscha*), and steelhead trout, a variant of rainbow trout (*Oncorhynchus mykiss*). Fillets from fall spawning runs are collected and analyzed for organic contaminants to assess human exposure.

The GLFMP, first started by the US Fish and Wildlife Service to assess DDT levels in Lake Michigan fish, evolved into a coordinated effort that consisted of a Cooperative Agreement between EPA GLNPO, the US Fish & Wildlife Service (now the National Biological Division of the US Geological Survey) and the Great Lakes states. In 2002, the GLNPO took over full time administration of the program.

This highly visible and successful program has provided the Great Lakes community with one of the most useful long-term data sets of organic contaminants on record, in addition to the fish and gull monitoring programs conducted by Canada. No comparable data sets for contaminant concentrations in water exist. Numerous reports and publications of the interpretation of these data resulted from EPA scientists involved in the GLFMP (De Vault 1984; De Vault 1985; De Vault *et al.* 1995; De Vault *et al.* 1988; De Vault *et al.* 1996; De Vault and Weishaar 1983; De Vault and Weishaar 1984; De Vault *et al.* 1986) The purpose of this paper is to present the most current data from the program, and use these data to illustrate differences in how contaminants are processed differently among lakes and within a lake. An interpretation of these data along with the other historic data to evaluate contaminant trends is being published elsewhere (Swackhamer and De Vault, 2005).

METHODS

Complete details of fish collection and contaminant analysis can be found at http://www.epa.gov/glindicators/fishtoxics/).

Fish Samples. Fish are collected by trawl from master sites from each lake in association with the BRD lake trout stock assessments (Figure 1). All fish samples were supplied by USGS BRD as frozen homogenates. The lake trout composites consist of 5 whole fish between 600-700 mm and the walleye composites (Lake Erie only) consist of 5 whole fish between 400-500 mm. A total of ten composites per lake per year are prepared. Occasionally insufficient numbers of fish are collected to meet this goal. Since 1984, one of the two master sites is sampled every other year, with the other site sampled in alternate years. Fall run coho, Chinook, and steehead trout (Lake Erie only) are collected by state fisheries personnel. Coho salmon stocking is declining in Lake Erie, and thus steelhead trout, a fall-spawning variant of rainbow trout, are substituted as a monitoring species. Three composites are prepared for each site each year consisting of 5 skin-on fillets, and are grouped to represent small, medium, and large fish. The records of length, weight, and sex of each fish in the composite were provided by USGS BRD.

Sample Extraction and Interference Removal for Organic Compounds. Samples are thawed and homogenized. A 2-3 g subsample (exact weight recorded) is mixed with anhydrous sodium sulfate and transferred quantitatively to a Soxhlet extractor charged with 150 mL of methanol (MeOH) and extracted for 4 hours. An aliquot of surrogate recovery standard solution (^{13}C-hexachlorobenzene, ^{13}C-lindane, ^{13}C-DDE, ^{13}C-chlordane, PCB-65, PCB-188) is added to each blank and sample. The MeOH is removed to a separatory funnel, and the Soxhlet charged with 150 mL dichloromethane (DCM) and extracted for an additional 18 hrs. The MeOH is extracted by adding 75 mL sodium chloride-saturated organic free water and back-extracting three times with hexane (3 x 25 mL). This extract is dried with anhydrous sodium sulfate and combined with the second Soxhlet extract, transferred to a Kuderna-Danish (KD) apparatus with Snyder column and reduced in volume and solvent-exchanged to hexane using a steam bath. The extract is brought to exactly 10 mL in hexane, and exactly 0.5 mL is removed for lipid analysis.

Lipids and other organic compounds must be removed from the extract to accurately detect and quantify the analytes of interest. Lipids are removed by passing the extracts over a column (1 x 30 cm) containing 13 g 6% deactivated alumina (60 mesh, w/w) and eluting with 3 x 30 mL

hexane. The eluate is collected in a KD and reduced in volume as before to approximately 10 mL. This extract is then placed on a column containing 4.5 g fully activated silica gel over 6 g 1% deactivated neutral alumina (w/w), with anhydrous sodium sulfate above and below each layer. The column is eluted with 3 x 30 mL hexane (Fraction 1). The column is further eluted with 3 x 30 mL 40%/60% DCM/hexane (Fraction 2). Each fraction is solvent exchanged to hexane and reduced to a volume of approximately 1 mL. At this time the extract is stored in a vial with teflon-lined cap and stored in a freezer. Prior to instrumental analysis, the extract is reduced to a few hundred microliters by gentle nitrogen gas stream, and the internal standard is added (PCB #204) to Fraction 1. A separate extraction of fish is required for Hg (see below).

Extract Instrumental Analysis. The analysis for PCBs is done first on Fraction 1. Once the data have been reviewed and found to be acceptable, then Fraction 1 and 2 are recombined and the remaining OC analyses are done on the combined extract. This is because of the high potential of interference from other compounds in PCB analyses. The other compounds do not experience interference from the PCBs and our experience has been that recoveries are improved if the two fractions are recombined.

PCB congeners are analyzed by gas chromatography with electron capture detection (GC-ECD). The method resolves and quantifies 110 congener or congener groups, and is similar to that used for the GLNPO Lake Michigan Mass Balance Study (Swackhamer and Trowbridge 1997) and previous Great Lakes PCB studies (Baker and Hites 2000; Skoglund *et al.* 1996; Swackhamer 1996). The GC (Hewlett Packard 5988) is equipped with an autosampler, large volume splitless injector, 60 m DB-5 column, Ni-63 ECD, and HP ChemStation data acquisition software.

The above method does not separate all of the toxic co-planar congeners, which preferentially bioaccumulate in fish relative to other PCBs (Trowbridge and Swackhamer 2002) and may be of interest particularly to the Great Lakes states' health authorities because of their human health significance (Safe 1994). We use another analysis for the co-planar congeners (Trowbridge and Swackhamer 2002), which is a modification of a method developed by (Schmidt and Hesselberg 1992) and uses gas chromatography mass spectrometry (GCMS) in electron capture negative ion mode (ECNI). This method utilizes the fact that GC/MS in the negative ion mode is very selective and sensitive to highly chlorinated compounds. AHH-inducing PCB congeners often co-elute with other congeners having a different number of

chlorine atoms, which allows them to be differentiated by GCMS-ECNI. The GC separation is the same, using helium as the carrier gas. The MS (Hewlett Packard 5988) has ChemStation and Aquarius acquisition software. The transfer line is maintained at 270 °C, the source temperature and pressure is 100 °C and 1 torr, the reagent gas is methane.

Toxaphene, chlordanes and nonachlors and all other organochlorines are analyzed by GCMS-ECNI. This technique is as sensitive as GC-ECD, but is far more accurate because it affords a means of eliminating interferences and providing confirmation from the resulting mass spectra. One injection and temperature program is used for the toxaphene, chlordanes, nonachlors, and a second injection and program is used to acquire the data for the remaining organochlorine compounds. The toxaphene method was originally developed by this investigator (Swackhamer *et al.* 1987) and subsequently modified by (Glassmeyer *et al.* 1999). We now use a modification of this method (Swackhamer, unpublished) that includes strict confirmation criteria to exclude non-toxaphene interferences.

A separate extraction is done for mercury. Fish tissue (0.2 to 1.0 g) is digested in a 5:2 ratio of concentrated nitric (HNO_3) and concentrated sulfuric (H_2SO_4) acids in Teflon digestion bombs in a conventional oven. Total mercury concentrations in the digestate are determined by cold vapor atomic fluorescence spectrometry (CVAFS) using a slight modification of the method of (Bloom and Crecelius 1983) in that BrCl is not added to the digestate.

The fraction lipid of each sample is determined gravimetrically by weighing exactly 1/10th of the extract of a known mass of fish tissue, taking to complete dryness, and reweighing to constant weight.

Quality control. A check sample is used to track reproducibility within the lab. This is a sample of lake trout prepared in the mid-1990s by USGS-BRD. The results of check sample analyses showed good reproducibility (CV = 13% ± 11%).

A series of 5 surrogate standards are added to every sample. Two PCB congeners (#65 and #188) not found in any Aroclor are added for assessing PCB recovery, and the stable isotopes (C-13 labeled) of HCB, lindane, DDE, and chlordane are used to assess the other analytes. The mean recoveries and standard deviations for all fish samples for each of the years 1999 and 2000 ranged from 66% to 111% for the suite of surrogates. There were no systematic differences in recoveries between species, or between years. All data are surrogate corrected.

A procedural blank is included with each set of six extractions. To be acceptable, any analytes noted in the blanks must be below the established detection limits. In all analyses, all blanks have been found acceptable.

Compounds from EPA's analyte list that were rarely or never detected in fish included pentachlorobenzene, lindane, aldrin, endrin, the o,p-substituted DDT family of compounds, p,p'-DDD, heptachlor, and heptachlor epoxide. Mirex was found only in Lake Ontario fish.

Statistics. Arithmetic means and 95% confidence limits are computed for the fish composites for each lake and each year. Composites of the same species from the same lake and year are considered field replicates. In general, values with a QA qualifier are not included; however, all data and statistics are reviewed. The means reported for coho, Chinook, and steelhead include only fish > 500 mm, which often means the "small" composite from coho collections was excluded. These smaller coho are usually only 1 year old and their contaminants are much lower than the adults.

Principal component analysis (PCA) was used for PCB congener concentrations in lake trout. PCA reduces the complexity of multivariate systems by creating a new coordinate system produced so as to maximize the amount of variability explained by individual variables. The relationship between the new variables (components) and the old variables allows for the determination of important behaviors in the dataset. Fifty congeners were used (ranging from PCB 31 to PCB 209), for 4600 data points, of which 19 (0.4%) were missing. In these cases, replacement values were estimated based on the average of concentrations of the analyte from fish from the same location.

RESULTS AND DISCUSSION

Concentrations

The mean values of all analytes for each year (1999 and 2000) are provided in Table 1. The complete data are publicly available and can be obtained by contacting the GLFMP project officer at GLNPO. Concentrations for all fish are reported as ng contaminant/g fish on a wet weight basis. All individual concentrations were corrected to the appropriate surrogate recovery, and reviewed carefully as described above. Lipid normalization does not reduce the variance

within a given species due to similar lipid values across lakes; hence the data are not lipid normalized.

The GLFMP was not designed to compare concentrations of contaminants across lakes, as the fish of a constant length are not the same ages across the lakes. However, some general conclusions can be drawn. Contaminants in lake trout and salmon are generally lowest in Lake Superior and highest in Lake Michigan, with a difference of approximately a factor of 3. Contaminant concentrations in Lake Huron and Lake Ontario are intermediate, with Huron usually lower than Ontario. This pattern is consistent with the historical and current sources of these compounds. Lake Michigan and Lake Ontario are the most impacted by development and industrial point sources and Lake Huron is less so; Lake Superior is dominated by inputs from the atmosphere. Exceptions to this are alpha-HCH and toxaphene which are greatest in Lake Superior (see below), and OCS and mirex which are greatest in Lake Ontario. The latter is due to a greater concentration of point sources of these compounds in the Lake Ontario basin compared to that of Lake Michigan.

Comparisons between lake trout and walleye should be done with extreme caution, as the two are not only different species, but also have very different foodchains. Contaminants in Lake Erie walleye are generally less than those found in lake trout from the other lakes, as would be expected due to their shorter foodchain. An exception is the PCB concentration, which is high relative to the other contaminants only at the Middle Bass Island site. This is likely due to the PCB-contaminated Detroit River.

Specific discussions of several compounds of interest that were routinely detected in lake trout and walleye follows.

PCBs. The PCB concentrations were lowest in Lake Superior (272 and 784 ng/g in 1999 and 2000) and greatest in Lake Michigan (1841 and 1614 ng/g in 1999 and 2000) which is consistent with previous data (e.g. DeVault et al. 1996). The significant differences in concentrations in Lakes Superior and Lake Erie between 1999 and 2000 are highly unlikely to be due to lake-wide differences between years, but rather differences between sites and/or populations of fish (see further discussion below).

In Lake Erie, PCB concentrations are greater in western basin sediments compared to the eastern basin (Marvin *et al.* 2002), and this gradient may be reflected in the walleye collected from those regions. While walleye are known to migrate throughout the lake, the collections

made in these years may be more representative of the local environment. These differences are not seen for other contaminants, which is consistent with the fact that the Detroit River historically had significant PCB point sources and currently has highly contaminated sediments. The movement of these sediments has created a PCB gradient from the western basin eastward, while other contaminants do not have the same well defined gradients.

DDT. The DDT components of interest are the p,p'-substituted compounds, and concentrations in lake trout are dominated by p,p'-DDE. On average, p,p'-DDT is expected to contribute approximately 10-30% of the total, but our data for this compound are not always consistent with this expectation. In particular, Lake Superior in 1999 and Lake Ontario in 2000 show higher than expected levels of DDT. These variations occur at one site within a lake but not the other, and thus cannot be due to annual changes in DDT long-range transport and deposition. Rather, this may reflect differences in the food webs at these sites. The contribution of DDD is negligible in all lakes and is usually below detection.

Concentrations of ∑DDT in lake trout were lowest in Lake Superior (167 and 567 ng/g in 1999 and 2000) which was similar to Lake Huron (504 and 557 ng/g in 1999 and 2000) and Lake Ontario (594 and 864 ng/g in 1999 and 2000). Concentrations were highest in Lake Michigan (883 and 1056 ng/g in 1999 and 2000). Concentrations in Lake Erie walleye were lower than in lake trout (95 and 85 ng/g in 1999 and 2000).

Dieldrin. Concentrations for dieldrin in lake trout ranged from a low of 21 and 31 ng/g in Lake Superior for the two years to a high of 94 and 90 ng/g in Lake Michigan. Concentrations in Lake Erie walleye were lower still, ranging from 9-12 ng/g.

Toxaphene, alpha-HCH. Concentrations of toxaphene and alpha-HCH are greatest in Lake Superior. Toxaphene in lake trout were 673 and 2490 ng/g in Lake Superior for the two years, and lowest in Lake Ontario (169-521 ng/g). Concentrations in walleye were lower still. The reasons for this are because the lakes all reached equilibrium with the atmosphere in the 1980s but Lake Superior is losing toxaphene at a much slower rate via volatilization and sedimentation than the other lakes due to its larger volume, lower productivity, and colder temperatures (Swackhamer *et al.* 1998; Swackhamer *et al.* 1999). Thus the water concentrations of toxaphene are greater than those in the other lakes, and the fish reflect the water (Glassmeyer *et al.* 1997). Toxaphene behaves this way because it has a higher vapor pressure and solubility than other

bioaccumulative organochlorines. Alpha-HCH also has a high relative vapor pressure and solubility, and thus it is logical that it would greater in Lake Superior fish.

Nonachlors and Chlordanes. In general, t-nonachlor was the most prevalent of these compounds, followed by c-nonachlor, oxychlordane, c-chlordane, and t-chlordane. T-nonachlor ranged from a high of 131-136 ng/g in Lake Michigan lake trout to less than half that value in the other lakes' trout. Although t-nonachlor was a minor component of the technical chlordane mixture, it is the least metabolized and predominates within the food web.

HCB. This compound is one of the most widely used organochlorine compounds in history, and is still commercially produced. Concentrations are similar in lake trout across the lakes, ranging from 7-25 ng/g. This pattern of similar concentrations indicates that the atmosphere may be the dominant source to all the lakes.

OCS and Mirex. Concentrations of OCS are greatest in Lake Ontario lake trout (10-20 ng/g), but found in concentrations ranging from 1-6 ng/g in the other lakes' trout. This may reflect the historic points sources of OCS to Lake Ontario. Mirex is detected only in Lake Ontario lake trout, a clear reflection of the point sources of mirex in the 1970s to this lake.

Mercury. Concentrations of mercury are similar across all fish from all lakes. Interestingly, this includes Lake Erie walleye, possibly due to the difference in factors that control mercury bioaccumulation compared to that of organochlorine compounds. Concentrations were generally 110-150 ng/g, with the exception of the Lake Superior 2000 fish which were 415 ng/g. This is consistent with the greater concentrations of most other contaminants at that site, as presented above and discussed further below. Furthermore, mercury concentrations in Lake Superior lake trout collected by the Minnesota Department of Natural Resources have been reported to have similar concentrations as these (Pat McCann, Minnesota Department of Health, personal communication).

PBDEs. A subset of the 1999 and 2000 fish were analyzed for a suite of PBDE congeners due to interest in adding this analyte to the routine monitoring list. Concentrations of the PBDE congeners were in the relative order 47>100=99>153=154>66. Concentrations were greatest in lake trout from Lake Michigan, followed by those from Lake Ontario and Lake Superior. Lake Huron lake trout had the lowest concentrations, and the data from both 1999 and 2000 was comparable. These data are comparable to those reported for other fish from the Great Lakes (Manchester-Neesvig *et al.* 2001; Zhu and Hites 2004). PBB-153 was found in the 1999 Lake

Huron lake trout at 1.4 ng/g and in Lake Ontario at 2.8 ng/g; the other composites were not analyzed due to a delay in receiving the analytical standard.

Differences Among Lakes and Between Sites Within a Lake

Differences between fish in the same lake but sampled in adjacent years are too close in time to determine trends, and are more likely due to differences in site characteristics. Note that in Lake Superior, the concentration of most contaminants are up to 3 times greater at the Apostles Islands site (2000) compared to the Keewenaw site (1999). Given that the lake trout are integrating over an 8-10 year time-period, there is no known possible mechanism that could increase the concentrations by factors of 2 or 3 over a one- or two-year time frame in the absence of a massive input of contaminants. It is possible that different populations of the same species within a lake may have different foodwebs. For example, one population may feed more on pelagic species, and another population may prefer benthic prey. These dietary differences would result in different contaminant concentrations, as the concentrations in prey control the concentrations in top predators (Thomann and Connolly 1984; Thomann *et al.* 1992). Differences between concentrations in lake trout from, for example, the two Lake Superior sites are therefore likely a result of real differences between populations of lake trout within Lake Superior, and not due to differences between years in contaminants in the lake as a whole. This is discussed further below.

Contaminant ratios within species were also examined in detail. The total PCB concentrations for lake trout are plotted against toxaphene concentrations in Figure 2. Both are banned, but the former had local, industrial sources, while the latter is an agricultural pesticide used historically in the southern United States on cotton, and entered the Great Lakes system largely by atmospheric deposition (Hoff *et al.* 1993). Figure 2 shows clusters for different sampling sites, confirming that there are indeed differences not only between lakes but between populations within a lake. We see that fish from Lakes Huron, Ontario, and Michigan generally have similar ratios, although there is no relationship between PCBs and toxaphene within a lake (probably because PCBs have a smaller range than toxaphene). Figure 3 includes the data for sport fish; we can see that Lake Superior is different from all other lakes. Within Lake Superior, the concentrations of toxaphene and PCBs are different among species and sites but the ratios are not, whether in lake trout or chinook. Fish from Lake Erie are not as similar to each other, even within a species, but generally fall on one side of the plot.

The Lake Superior ratios of toxaphene to PCBs are different from other lakes because Lake Superior has the lowest PCB concentrations but the greatest toxaphene concentrations of any of the lakes, as discussed above. This difference in sources and differences in processing contaminants by Lake Superior is thus reflected in very different ratios.

Differences in PCB Congeners

The concentrations of approximately 50 PCB congeners in lake trout were also compared to each across the different sampling sites using principal component analysis (PCA). Figure 4 shows the scores for the first two components plotted against each other. Component 1 explained the majority of the variability (68%) and had approximately equal loadings from almost every congener. Component 1 can therefore be used as a surrogate for total PCB concentration; indeed, a plot of Component 1 scores versus total PCBs reveals a significant linear correlation with an R^2 value greater than 0.98. The loadings for Component 2 are shown in Figure 5; this component can be used as a surrogate for degree of chlorination. At all sites except Saugatuck (which has too little variation in total PCBs to see a trend), the fish within that site with more total PCBs had a greater contribution from the more chlorinated PCBs (not shown).

In Lake Superior, this trend is quite striking, as shown by the regression line in Figure 4 for all Lake Superior lake trout. The two sites occupy different areas on this plot, with PCB concentrations being greater in Apostle Islands fish compared to Keweenaw fish. These site differences may be due to food chain differences between these two populations. Gut analyses indicate that lake trout from the Apostle Islands consume up to 20% of their diet as burbot, while those from Keweenaw rarely consume burbot (T. Hrabik, University of Minnesota – Duluth, personal communication). Because burbot consume coregonids, the net effect of this would be to add another trophic level in the Apostle Islands lake trout foodchain, causing an increase in PCB congeners, with a biomagnification of the more chlorinated congeners and further metabolism of the less chlorinated congeners. The greater contribution of chlorination with increasing PCB concentrations is a highly significant relationship within Lake Superior (Fig. 4, $r^2 = 0.98$). This strong relationship is not explained by length, weight, or gender data from the fish making up the composites. Perhaps it simply represents a gradient of diet among the fish from these sites.

Figure 4 also shows that two sites have significantly different Component 2 scores than all the rest: Sturgeon Bay (Lake Michigan) has a PCB profile weighted towards the less chlorinated homologues, while Apostle Islands (Lake Superior) is the opposite. This is illustrated more clearly in Figure 6, which shows the PCB homologue profiles for Sturgeon Bay, Apostle Islands, and the means for all other sites.

The enhancement of less chlorinated PCBs in Sturgeon Bay lake trout is readily apparent when each congener profile is normalized to the fraction of heptachloro PCBs (Figure 7). This figure suggests that Sturgeon Bay fish have a "general" Lake Michigan signal (Saugatuck) plus an additional signal. In other words, the relative amounts of hexa- through nonachloro PCBs is similar at the two sites, but Sturgeon Bay has excess di- through pentachloro PCBs. If we subtract the Saugatuck signal from the Sturgeon Bay signal, we calculate the "difference profile" shown as solid bars in Figure 8 as the 'extra' PCB contamination for the Sturgeon Bay fish.

Madenjian et al. (1999) showed that PCB concentrations observed in lake trout collected in 1994 from Saugatuck were greater than those from Sturgeon Bay, and that the differences in PCB concentration could be explained by diet preference differences. We would expect food web effects to result in enhancement of the more highly chlorinated congeners in fish with greater PCB concentrations (in the case of the 1999-2000 data, this would correspond to the Sturgeon Bay fish). The greater proportion of the *less* chlorinated congeners in the fish from Sturgeon Bay therefore implies an additional source of PCBs rather than food web effects.

We explored the hypothesis that Green Bay could be the source of these PCBs. The Fox River, historically the location of a high density of paper mills that recycled carbonless copy paper containing Aroclor 1242 (Kovatch 2002), is a major source of PCBs to Green Bay (U.S. Environmental Protection Agency 2005). Sediments from the Fox River and Green Bay have very different PCB profiles than sediments in Lake Michigan in general (Cacela *et al.* 2002) and near Saugatuck specifically (Burkhard *et al.* 2004). Biota-sediment accumulation factors (BSAF) for Saugatuck lake trout have been calculated on a congener basis (Burkhard *et al.* 2004). If we assume that the BSAF are very similar for fish in northern Lake Michigan, then we can multiply the Green Bay sediment congener profile by the congener-specific BSAF (re-calculated using only data for lake trout six years of age, on a wet-weight basis) to calculate a hypothetical PCB profile of a lake trout living in an ecosystem with Green Bay sediment, shown as the white bars in Figure 8. The calculated profile is displayed in Figure 8 juxtaposed with the

"difference profile"; congeners for which the difference in hepta-PCB normalized abundance between Saugatuck and Sturgeon Bay fish was less than 5% were not included. Inspection shows they are fairly similar in pattern, and so the difference in PCB profiles between lake trout from Saugatuck and lake trout from Sturgeon Bay (Figure 6) is consistent with contamination from Green Bay, and, originally, the Fox River. Using this approach, approximately 10-15% of PCB mass in Sturgeon Bay lake trout can be attributed to the Fox River.

PBDE Congener Differences Among Lakes

We also examined the relative contributions and absolute concentrations of PBDE congeners. Contamination patterns were similar to PCBs, in that fish from Lake Michigan had the most PBDEs and fish from Lake Superior had the least. Interestingly, Lake Superior also has different congener profiles for PBDEs. Figure 9 shows a plot of BDE 99 versus BDE 47. Lake Superior has a very different ratio (approximately 2:3) compared to all other sites (approximately 1:5). This is confirmed by analysis of the same fish composites by another lab (Zhu and Hites 2004) and similar to data from other lake trout samples (Luross *et al.* 2002). The sediments also show a similar difference for Lake Superior (Song *et al.* 2004; Song *et al.* 2005; Zhu and Hites 2005), but the atmospheric samples do not (Strandberg *et al.* 2001). This implies there is a difference in internal PBDE processing in Lake Superior compared to all the other lakes. Some species of fish have been shown to degrade BDE 99 to BDE 47 (Stapleton *et al.* 2004). The greater contributions of BDE 99 in Lake Superior fish could be attributed to less biotransformation occurring in this colder lake. However, we note that lake trout live below the thermocline in all the lakes, and the hypolimnion of the lakes is the same temperature (the colder mean temperature of Lake Superior is due to its cold epilimnion during the stratified period). Thus biotransformation rates should be similar across lakes.

Interestingly, the PCBs show similar behavior. The ratio of PCB 99 to PCB 47 for all Lake Superior lake trout is approximately 9:1, but for all other lakes it is about 7:2. In other words, for a given PCB 47 concentration, the PCB 99 concentration will be about 2.6 times higher in Lake Superior than all the other lakes. Likewise, for PBDEs, the BDE 99 concentration in Lake Superior will be about 3.3 times higher in Lake Superior compared to all other lakes. This implies, if we assume property differences vary to the same degree in PCBs and PBDEs, that the differences in congener profiles for both PCBs and PBDEs are driven by physical/chemical properties and not source differences or biodegradation.

Previous work has shown that the organisms of the lowest trophic level, phytoplankton, are not necessarily in equilibrium with the aqueous phase in regards to PCBs (Skoglund *et al.* 1996; Swackhamer and Skoglund 1993). If growth is fast, kinetics limit the uptake of the more chlorinated PCBs. If growth is slow, however, all congeners can reach equilibrium between the water and the phytoplankton. Using a range of estimates for phytoplankton growth rates, a previously published model (Skoglund *et al.* 1996) predicts that for a given concentration of PCB 47, the PCB 99 concentration will be around 1.3-2.8 times higher in Lake Superior compared to the other Great Lakes. Congener 99 (penta-substituted) has a greater K_{ow} than 47 (tetra-substituted), and takes a longer time to reach equilibrium than 47. Given the same source loading, a system with a high growth rate will have a lower concentration of 99 in phytoplankton (and thus the rest of the food web) than in a system with slow growth rates. Lake Superior has slower phytoplankton growth rates than any of the other Great Lakes, due to its significantly colder summertime temperatures (Government of Canada and United States Environmental Protection Agency 1995). It follows that contaminants in Lake Superior may be closer to or achieve equilibrium between phytoplankton and the aqueous phase. Consequently, Lake Superior phytoplankton should have a greater proportion of the more highly chlorinated PCBs (and by analogy the more highly brominated PBDEs), and this difference in PCB congener profile should be reflected in the sediments and food web – exactly what the observations show.

In conclusion, the most current data available from the GLFMP are presented. These data shed light on how differences in sources affect concentrations of contaminants in fish, but also how differences in how the lakes process chemicals internally due to physical characteristics and food web characteristics can affect concentrations of contaminants in fish.

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Table 1. Mean (± 95% confidence limits) concentrations of PCBs and organochlorine pesticides in Great Lakes fish samples. na= not analyzed or available, nd = non-detect, N is the number of composites analyzed. Means for sport fish exclude any composites with mean fish length <500 mm.

Year	Species	N	Site	Lake	Total PCBs	HCB	α-HCH	Dieldrin	OCS	p,p-DDE	p,p-DDT
1999	Lake Trout	10	Keweenaw	Superior	272±55	7.4±0.8	11±1.3	21±4.6	nd	92±20	93±42
2000	Lake Trout	10	Apostle Isl	Superior	784±150	15±1.4	7.7±2.3	31±7.2	6.2±1.0	361±87	175±79
1999	Lake Trout	10	Port Austin	Huron	918±86	12±1.0	2.2±0.3	36±5.1	4.0±0.9	376±54	78±32
2000	Lake Trout	10	Rockport	Huron	779±104	12±1.4	2.3±0.3	32±5.5	2.2±0.3	347±53	181±28
1999	Lake Trout	9	Sturgeon Bay	Michigan	1865±256	15±2.8	2.5±0.3	96±7.6	1.6±0.4	612±109	319±125
2000	Lake Trout	10	Saugatuck	Michigan	1614±92	12±1.5	1.6±0.3	90±18	1.8±0.6	801±84	246±90
1999	Lake Trout	10	N Hamlin	Ontario	1294±125	24±2.9	3.2±0.4	64±12	19.5±4.6	484±62	137±73
2000	Lake Trout	10	Oswego	Ontario	1174±116	19±1.5	2.6±0.5	45±9	9.6±1.3	437±36	394±134
1999	Walleye	7	Dunkirk	Erie	569±163	3.7±1.4	nd	8.7±0.9	2.5±1.5	85±44	nd
2000	Walleye	6	Middle Bass Isl	Erie	1241±295	3.2±.28	nd	12±1.7	5.8±1.3	67±11	nd
1999	Steelhead	3	Grand R	Erie	365±64	2.8±0.3	nd	8.3±0.7	nd	26±8.1	nd
1999	Steelhead	3	Trout Run	Erie	498±71	4.8±1.5	nd	14±4.3	1.9±0.5	48±11	nd
2000	Steelhead	3	Grand R	Erie	491±184	na	na	na	na	na	na
1999	Chinook	3	Pike's Cr	Superior	159±17	4.8±0.5	1.5±0.2	13±5.0	3.6±3.6	45±1.8	nd
1999	Chinook	3	French R	Superior	233±34	5.9±1.0	nd	15±0.7	1.8	59±7.5	nd
1999	Chinook	3	St Joseph R	Michigan	780±39	4.1±0.3	2.4	19±4.0	nd	382±31	38±10
1999	Chinook	3	Platte R	Michigan	1037±445	4.0±1.0	nd	24±15	1.8	540±359	
1999	Chinook	3	Grand R	Michigan	1267±189	3.8±1.3	nd	17±0.6	nd	565±168	38±18
1999	Chinook	3	Trail Cr	Michigan	756±140	1.8±0.2	13	18±2.4	nd	317±45	26±2.8
1999	Chinook	3	Root R	Michigan	863±57	3.1±1.5	nd	16±2.9	2.0±0.6	456±63	30±6.8
1999	Chinook	3	Thompson Cr	Michigan	1053±267	3.5±1.3	nd	7.8±2.5	1.6±0.01	518±124	33±17
1999	Chinook	3	Salmon Hchry	Ontario	906±291	5.8±1.2	nd	6.7±1.6	10±1.7	360±137	49±22
1999	Chinook	3	Swan R	Huron	1161±845	3.6±0.2	nd	16±0.5	nd	364±48	27±5.4
1999	Chinook	3	Au Sable	Huron	433±104	2.6±0.6	29	6.7±0.4	1.9±0.5	175±45	26±8.2
2000	Chinook	3	Swan R	Huron	719±270	3.8±0.7	nd	16±11	nd	268±117	94±56
2000	Coho	3	French R	Superior	38	na	na	na	na	na	na
2000	Coho	3	Kewaunee R	Michigan	649±35	3.0±0.1	nd	8.4±1.7	nd	274±3.5	35±10
2000	Coho	3	Trail Cr	Michigan	463±68	2.8±0.3	nd	10±1.7	nd	187±26	12±24
2000	Coho	3	Thompson Cr	Michigan	450±35	2.2±0.02	nd	10±2.2	nd	206±23	16±14
2000	Coho	3	Grand R	Michigan	581±80	2.7±1.0	nd	7.4±2.0	nd	259±70	12±23
2000	Coho	3	St Joseph R	Michigan	613±81	na	na	na	na	na	na
2000	Coho	3	Platte R	Michigan	714±116	na	na	na	na	na	na
2000	Coho	3	Root R	Michigan	826±51	na	na	na	na	na	na
2000	Coho	3	Black R	Huron	385	na	na	na	na	na	na

Table 1, Continued.

Year	Species	N[a]	Site	Lake	Toxaphene	*t*-Nonachlor	*c*-Nonachlor	*t*-Chlordane	*c*-Chlordane
1999	Lake Trout	10	Keweenaw	Superior	673±125	33±8.0	17±3.3	4.7±1.3	7.4±1.6
2000	Lake Trout	10	Apostle Isl	Superior	2221±440	146±36	102±24	18±6.1	36±6.5
1999	Lake Trout	10	Port Austin	Huron	467±150	58±9.3	25±4.6	6.5±1.7	16±2.8
2000	Lake Trout	10	Rockport	Huron	676±98	48±11	33±7.0	11±2.4	16±4.0
1999	Lake Trout	9	Sturgeon Bay	Michigan	813±225	122±26	66±7.0	34±8.7	41±4.2
2000	Lake Trout	10	Saugatuck	Michigan	987±172	138±26	72±9.9	22±7.0	47±9.4
1999	Lake Trout	10	N Hamlin	Ontario	169±29	60±8.7	23±4.3	6.3±0.5	17±3.0
2000	Lake Trout	10	Oswego	Ontario	489±125	47±7.5	30±3.1	11±4.1	21±2.2
1999	Walleye	7	Dunkirk	Erie	31±18	9.1±6.3	5.7±0.8	4.8±2.0	9.6±5.5
2000	Walleye	6	Middle Bass Isl	Erie	189±86	7.8±0.8	6.7±1.2	5.3±1.0	6.7±0.8
1999	Steelhead	3	Grand R	Erie	nd	8.0±4.6	2.8±0.7	1.8	3.4±0.8
1999	Steelhead	3	Trout Run	Erie	14±8	10±4.5	4.9±1.6	3.7±0.5	6.4±1.5
2000	Steelhead	3	Grand R	Erie	na	na	na	na	na
1999	Chinook	3	Pike's Cr	Superior	376±33	21±3.2	10±1.4	3.4±0.1	4.5±0.8
1999	Chinook	3	French R	Superior	417±80	26±4.4	12±1.9	3.7±0.7	5.1±1.5
1999	Chinook	3	St Joseph R	Michigan	311±55	60±6.7	25±1.9	7.4±0.3	11±1.2
1999	Chinook	3	Platte R	Michigan	391±99	86±34	40±20	7.9±2.2	14±3.8
1999	Chinook	3	Grand R	Michigan	367±33	96±11	44±10	14±7.5	17±1.5
1999	Chinook	3	Trail Cr	Michigan	240±10	51±7.4	22±1.6	6.3±0.5	9.1±1.1
1999	Chinook	3	Root R	Michigan	186±6.8	66±7.4	28±5.4	6.9±0.4	12±0.5
1999	Chinook	3	Thompson Cr	Michigan	191±55	72±18	31±8.5	5.9±1.6	12±3.8
1999	Chinook	3	Salmon Hchry	Ontario	81±36	35±12	15±4.6	2.7±0.6	6.5±1.5
1999	Chinook	3	Swan R	Huron	125±43	45±13	17±3.9	5.6±1.1	10±2.4
1999	Chinook	3	Au Sable	Huron	86±21	31±6.5	12±2.1	3.4±1.5	5.4±1.7
2000	Chinook	3	Swan R	Huron	238±139	49±15	29±19	5.0±0.9	11±2.1
2000	Coho	3	French R	Superior	na	na	na	na	na
2000	Coho	3	Kewaunee R	Michigan	202±10	27±3.8	12±0.8	3.8±0.2	8.7±1.4
2000	Coho	3	Trail Cr	Michigan	199±5.8	20±0.4	10±1.1	3.2±0.1	7.1±0.01
2000	Coho	3	Thompson Cr	Michigan	176±20	26±3.5	11±0.7	3.7±0.1	8.6±1.6
2000	Coho	3	Grand R	Michigan	191±15	33±0.5	14±0.5	4.5±0.3	10±0.9
2000	Coho	3	St Joseph R	Michigan	na	na	na	na	na
2000	Coho	3	Platte R	Michigan	na	na	na	na	na
2000	Coho	3	Root R	Michigan	na	na	na	na	na
2000	Coho	3	Black R	Huron	na	na	na	na	na

Table 1, Continued.

Year	Species	N[a]	Site	Lake	BDE 47	BDE 66	BDE 99	BDE 100	BDE 153	BDE 154	Hg
1999	Lake Trout	10	Keweenaw	Superior	na	na	na	na	na	na	123±21
2000	Lake Trout	10	Apostle Isl	Superior	79±21	3.9±15	53±14	19±4.6	8.8±3.1	16±4.1	433±76
1999	Lake Trout	10	Port Austin	Huron	32±7.7	0.7±0.2	7.8±2.2	6.5±1.9	1.4±0.4	2.0±0.9	144±20
2000	Lake Trout	10	Rockport	Huron	59±13	1.0±0.7	13±1.7	12±2.9	2.1±0.8	7.1±1.4	144±18
1999	Lake Trout	9	Sturgeon Bay	Michigan	na	na	na	na	na	na	127±8.8
2000	Lake Trout	10	Saugatuck	Michigan	228±82	3.7±1.4	48±16	45±13	11±4.2	19±7.1	146±18
1999	Lake Trout	10	N Hamlin	Ontario	na	na	na	na	na	na	123±8.5
2000	Lake Trout	10	Oswego	Ontario	144±38	2.4±0.7	34±13	24±9.2	10±2.7	13±4.9	115±15
1999	Walleye	7	Dunkirk	Erie	na	na	na	na	na	na	124±37
2000	Walleye	6	Middle Bass Isl	Erie	32±7.9	nd	5.9±1.8	7.8±1.9	2.6±1.5	2.4±0.9	114±11
1999	Steelhead	3	Grand R	Erie	na	na	na	na	na	na	na
1999	Steelhead	3	Trout Run	Erie	na	na	na	na	na	na	na
2000	Steelhead	3	Grand R	Erie	na	na	na	na	na	na	na
1999	Chinook	3	Pike's Cr	Superior	na	na	na	na	na	na	na
1999	Chinook	3	French R	Superior	na	na	na	na	na	na	na
1999	Chinook	3	St Joseph R	Michigan	na	na	na	na	na	na	na
1999	Chinook	3	Platte R	Michigan	na	na	na	na	na	na	na
1999	Chinook	3	Grand R	Michigan	na	na	na	na	na	na	na
1999	Chinook	3	Trail Cr	Michigan	na	na	na	na	na	na	na
1999	Chinook	3	Root R	Michigan	na	na	na	na	na	na	na
1999	Chinook	3	Thompson Cr	Michigan	na	na	na	na	na	na	na
1999	Chinook	3	Salmon Hchry	Ontario	na	na	na	na	na	na	na
1999	Chinook	3	Swan R	Huron	na	na	na	na	na	na	na
1999	Chinook	3	Au Sable	Huron	na	na	na	na	na	na	na
2000	Chinook	3	Swan R	Huron	54±36	2.3±1.9	24±10	13	5.4±3.8	6.0±3.8	na
2000	Coho	3	French R	Superior	na	na	na	na	na	na	na
2000	Coho	3	Kewaunee R	Michigan	57±5.7	nd	15±2.4	12±2.8	4.9±10	5.0±11	121±2.9
2000	Coho	3	Trail Cr	Michigan	33±5.1	nd	4.4±8.7	3.6±7.0	nd	nd	125±4.9
2000	Coho	3	Thompson Cr	Michigan	35±6.1	nd	10±2.3	7.9±0.5	nd	nd	126±20
2000	Coho	3	Grand R	Michigan	25	nd	9.3	5.6	nd	nd	125
2000	Coho	3	St Joseph R	Michigan	na	na	na	na	na	na	na
2000	Coho	3	Platte R	Michigan	na	na	na	na	na	na	na
2000	Coho	3	Root R	Michigan	na	na	na	na	na	na	na
2000	Coho	3	Black R	Huron	na	na	na	na	na	na	na

Figure Captions

Figure 1. Sampling locations for lake trout and walleye. Point marked with a circle were sampled in 1999; those with squares were sampled in 2000.

Figure 2. Relationship between PCB and toxaphene concentrations (ng/g wet weight) in lake trout from lakes Ontario, Michigan, Huron, and Superior from 1999 (open symbols) and 2000 (filled symbols).

Figure 3. Relationship between PCB and toxaphene concentrations in all species. Lines indicate PCB:toxaphene ratios.

Figure 4. PCA Component scores of lake trout from lakes Ontario, Michigan, Huron, and Superior from 1999 and 2000. The percent of the variance explained by each component is in parentheses. Component 1 is strongly correlated to total PCB concentrations; total PCB concentrations can therefore be determined using the secondary x-axis above. Component 2 is related to the degree of chlorination of the PCBs; see Figure 4. The line is a regression through all Lake Superior lake trout data ($R^2 = 0.98$).

Figure 5. Component 2 loadings for PCA of lake trout PCB congener concentrations.

Figure 6. PCB homologue profiles for lake trout at Saugatuck, Apostle Islands, and the mean of all other sites. Error bars indicate standard deviations.

Figure 7. PCB homologue groups normalized to heptachloro-biphenyls for lake trout from two sites in Lake Michigan.

Figure 8. Comparison of observed "difference profile" between Sturgeon Bay and Saugatuck lake trout with the lake trout PCB profile predicted from literature BSAF and Green Bay sediments. Only congeners with more than a 5% difference in hepta-PCB normalized abundance between Saugatuck and Sturgeon Bay fish were used for this graph.

Figure 9. Comparison of BDE congener ratios in lake trout and walleye. Lines indicate BDE 99:47 ratios of 2:3 and 1:5.

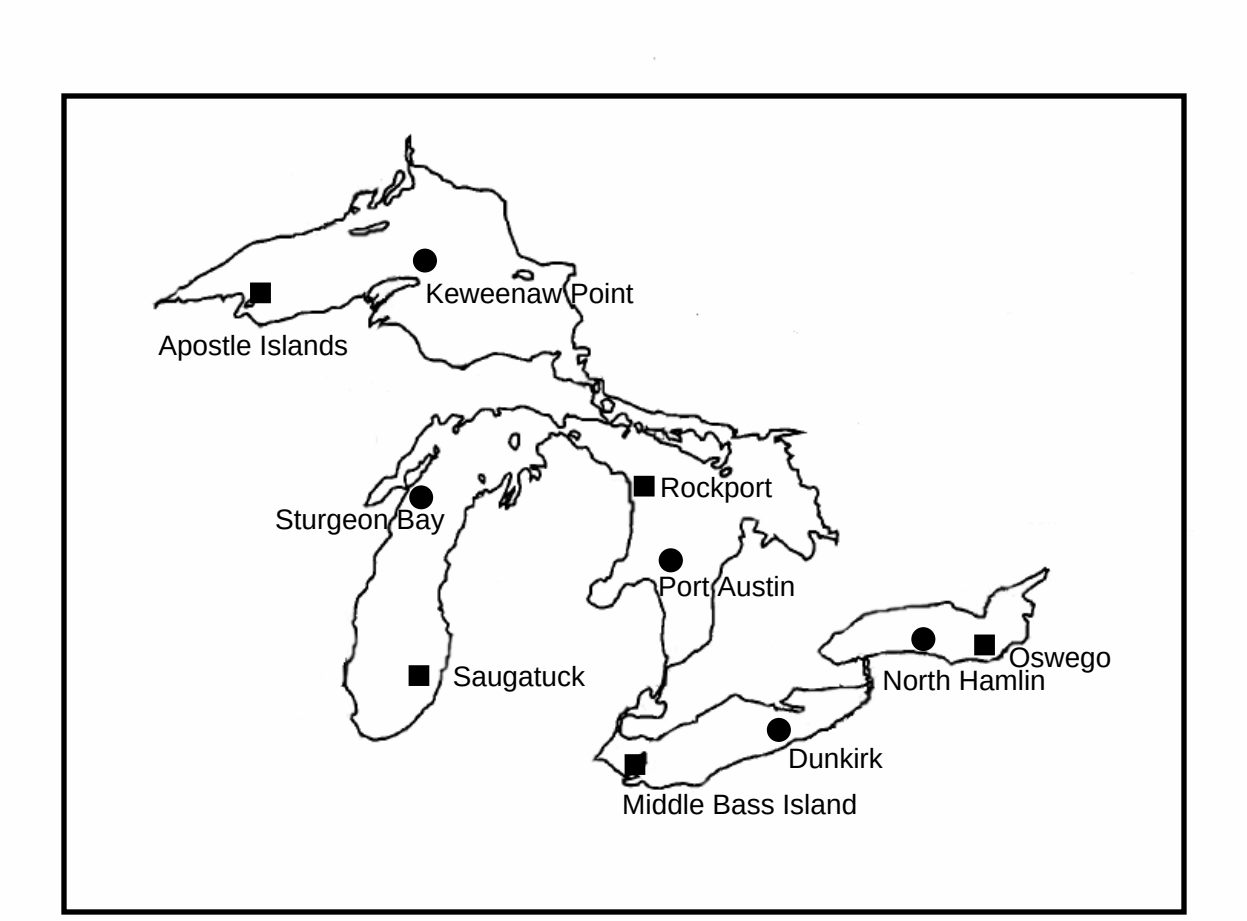
Keweenaw Point
Apostle Islands
Rockport
Sturgeon Bay
Port Austin
Oswego
North Hamlin
Saugatuck
Dunkirk
Middle Bass Island

FIG 1

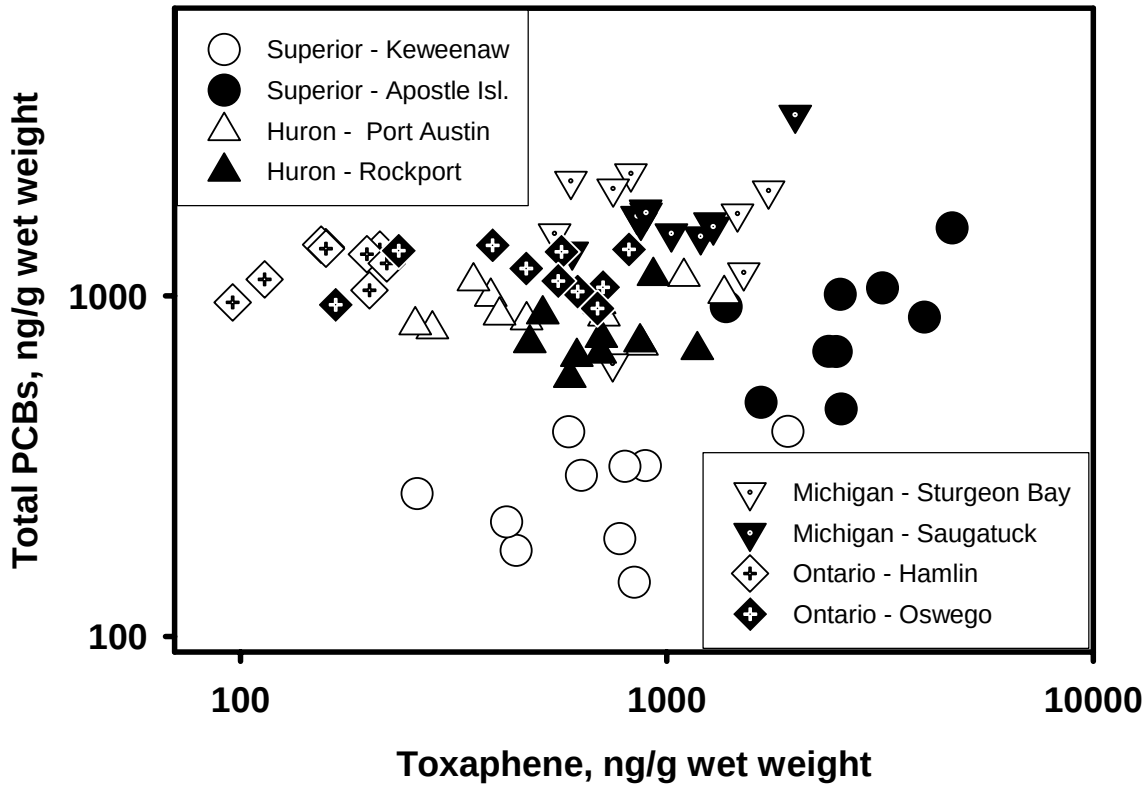
Superior - Keweenaw
Superior - Apostle Isl.
Huron - Port Austin
Huron - Rockport
Michigan - Sturgeon Bay
Michigan - Saugatuck
Ontario - Hamlin
Ontario - Oswego
Total PCBs, ng/g wet weight
1000
100
100
1000
10000
Toxaphene, ng/g wet weight

FIG 2

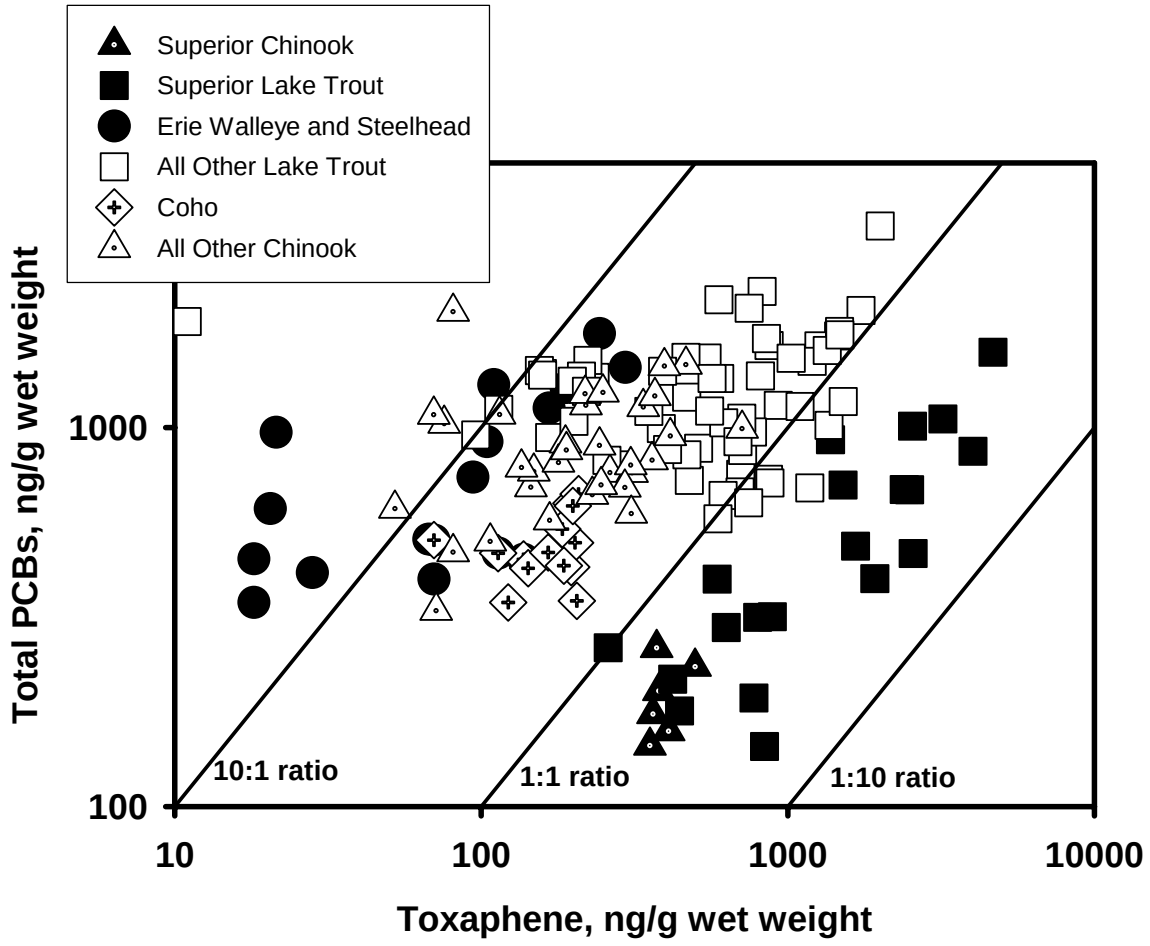
Superior Chinook
Superior Lake Trout
Erie Walleye and Steelhead
All Other Lake Trout
Coho
All Other Chinook
Total PCBs, ng/g wet weight
1000
100
10:1 ratio
1:1 ratio
1:10 ratio
10
100
1000
10000
Toxaphene, ng/g wet weight

FIG 3

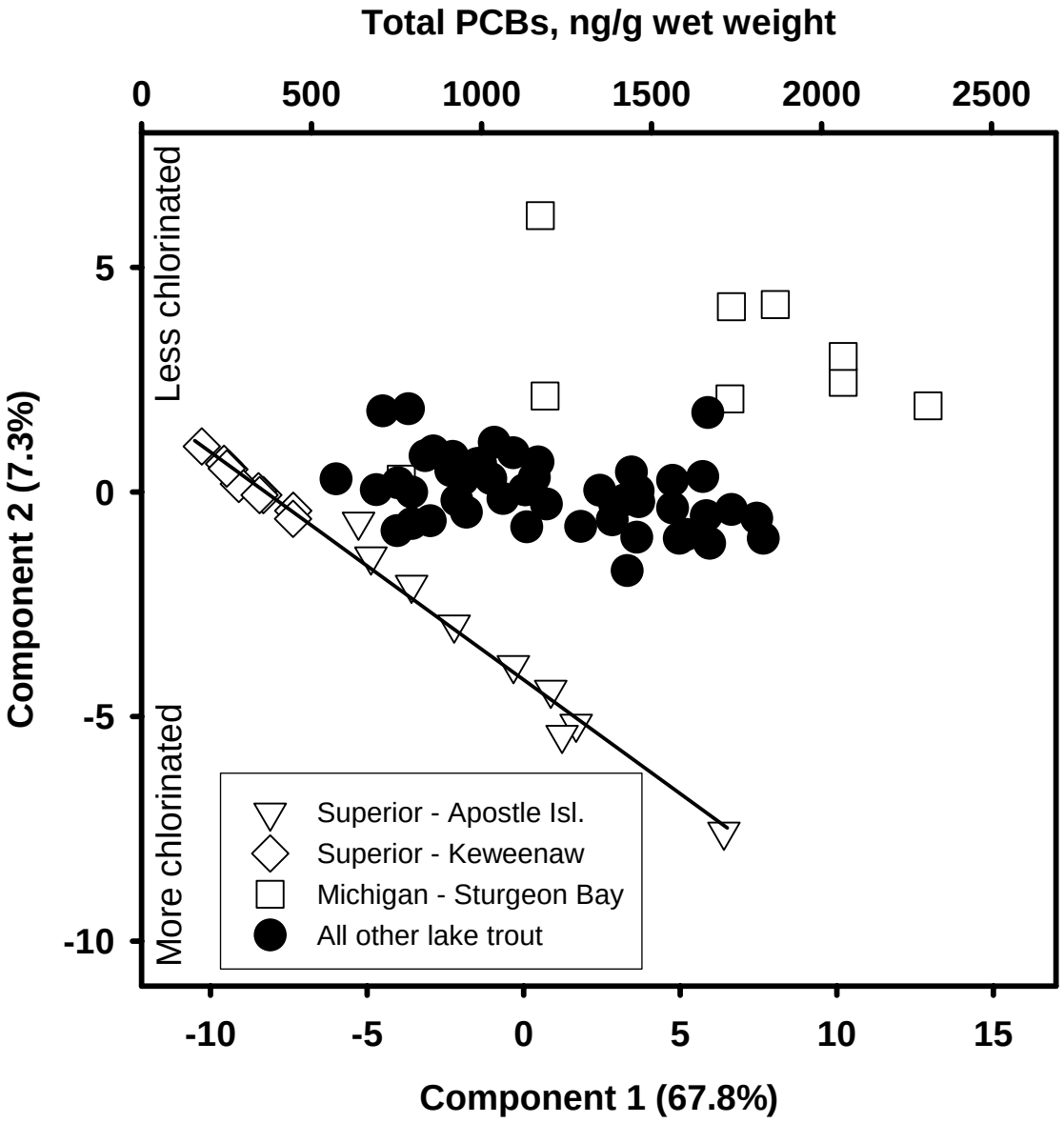
Total PCBs, ng/g wet weight
0
500
1000
1500
2000
2500
Less chlorinated
More chlorinated
5
0
-5
-10
Component 2 (7.3%)
-10
-5
0
5
10
15
Component 1 (67.8%)
Superior - Apostle Isl.
Superior - Keweenaw
Michigan - Sturgeon Bay
All other lake trout

FIG 4

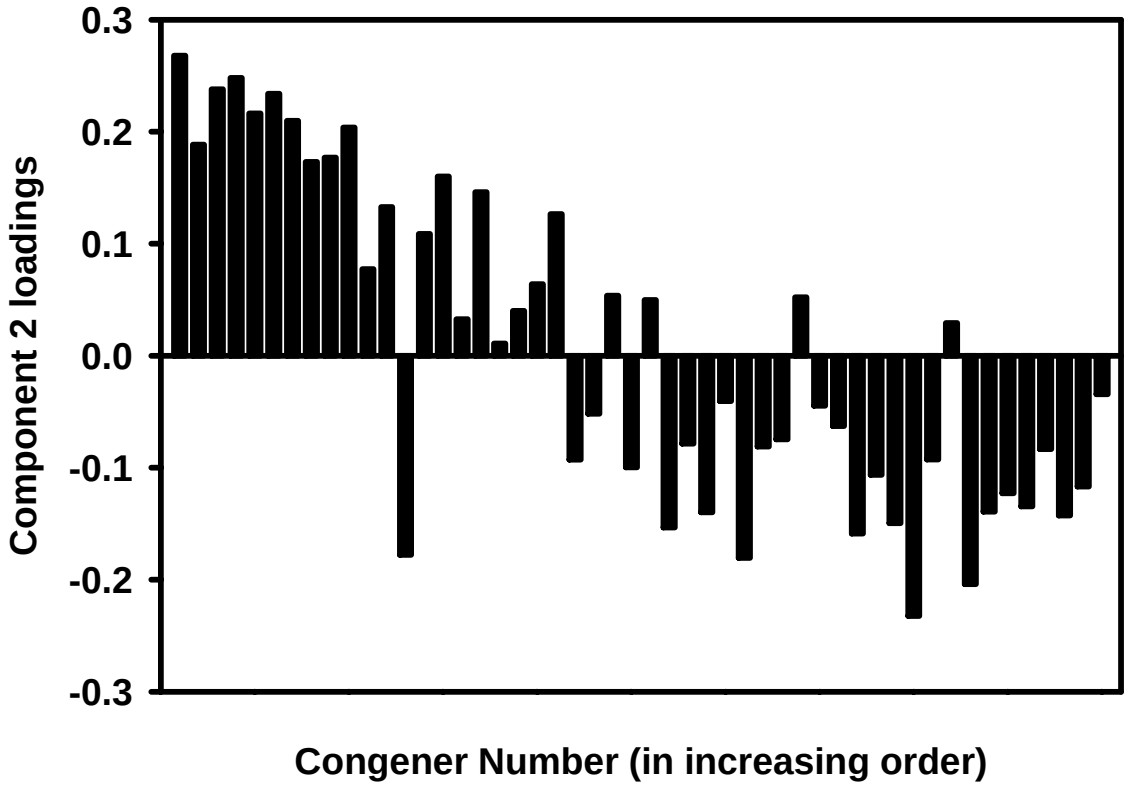
0.3
0.2
0.1
0.0
-0.1
-0.2
-0.3
Component 2 loadings
Congener Number (in increasing order)

FIG 5

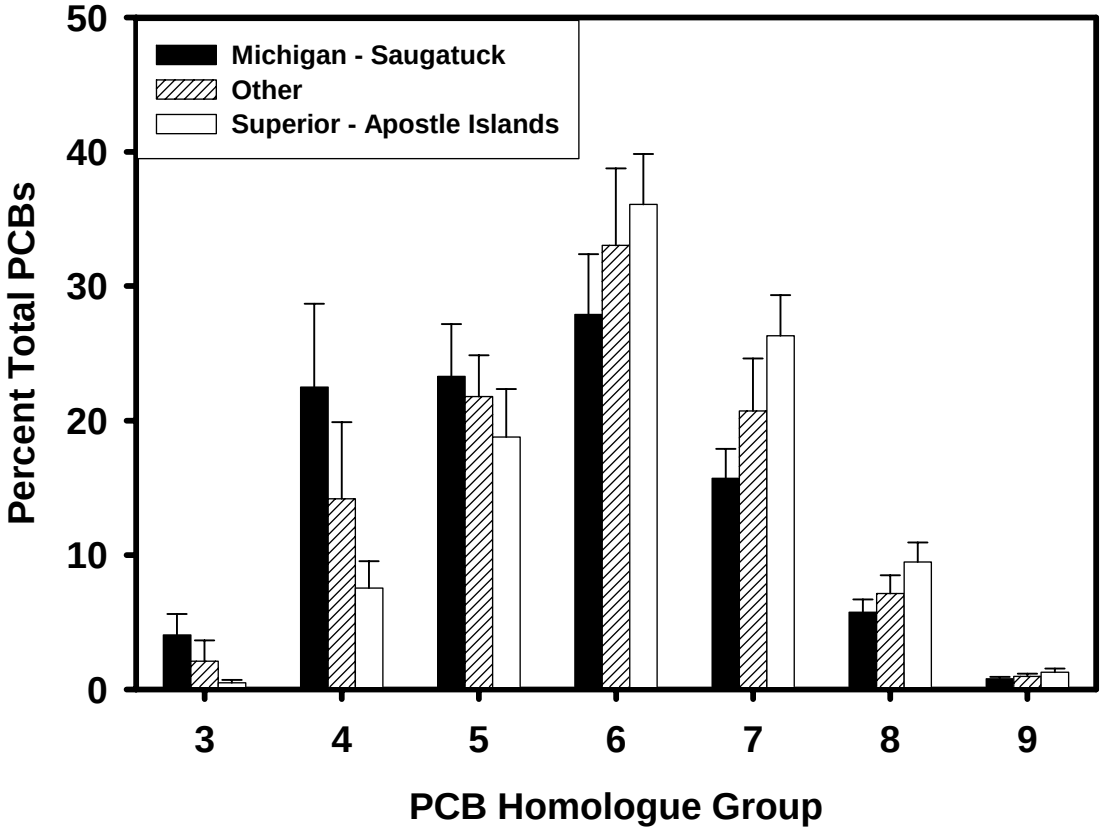
Michigan - Saugatuck
Other
Superior - Apostle Islands
Percent Total PCBs
50
40
30
20
10
0
3
4
5
6
7
8
9
PCB Homologue Group

FIG 6

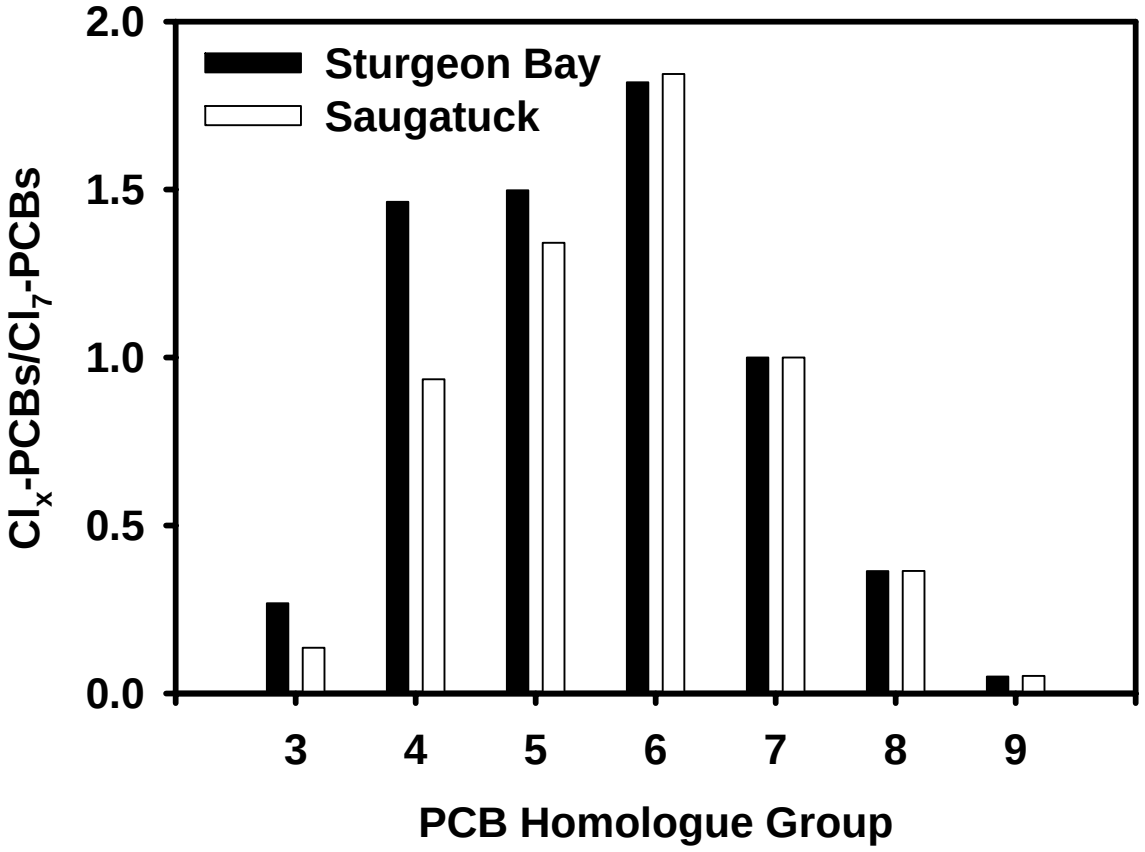
Sturgeon Bay
Saugatuck
2.0
1.5
1.0
0.5
0.0
Cl_x-PCBs/Cl_7-PCBs
3
4
5
6
7
8
9
PCB Homologue Group

FIG 7

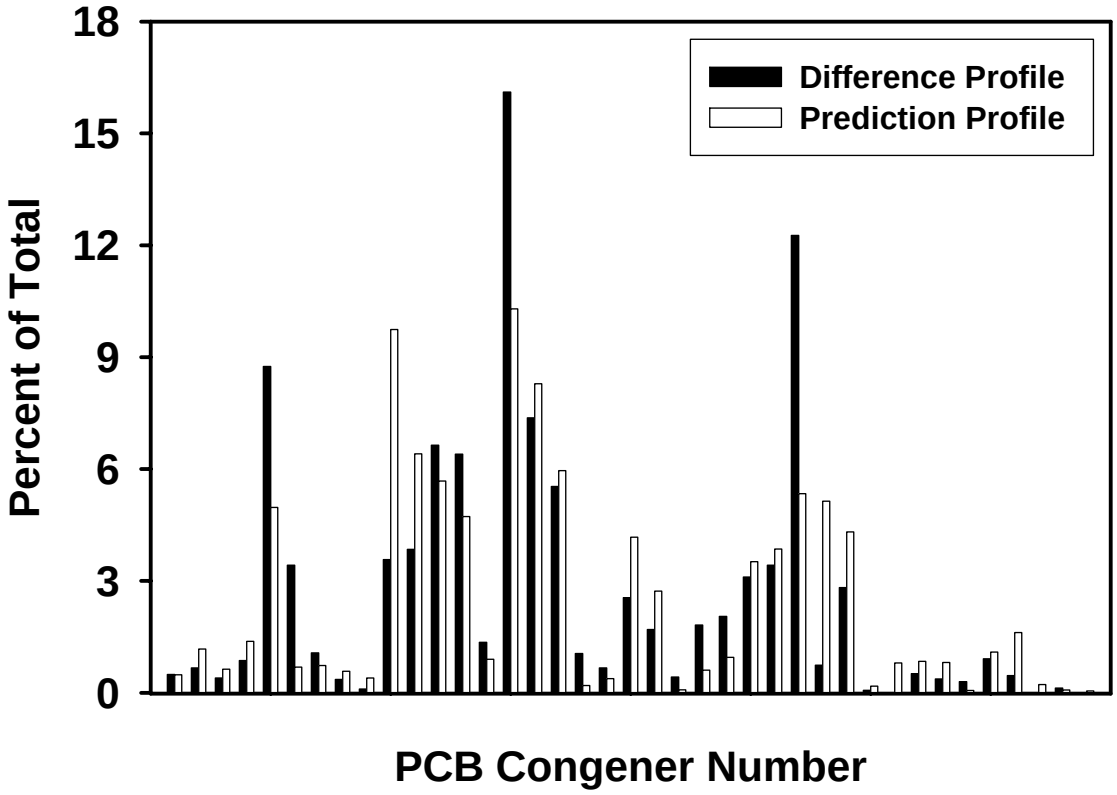
18
15
12
9
6
3
0
Percent of Total
Difference Profile
Prediction Profile
PCB Congener Number

FIG 8

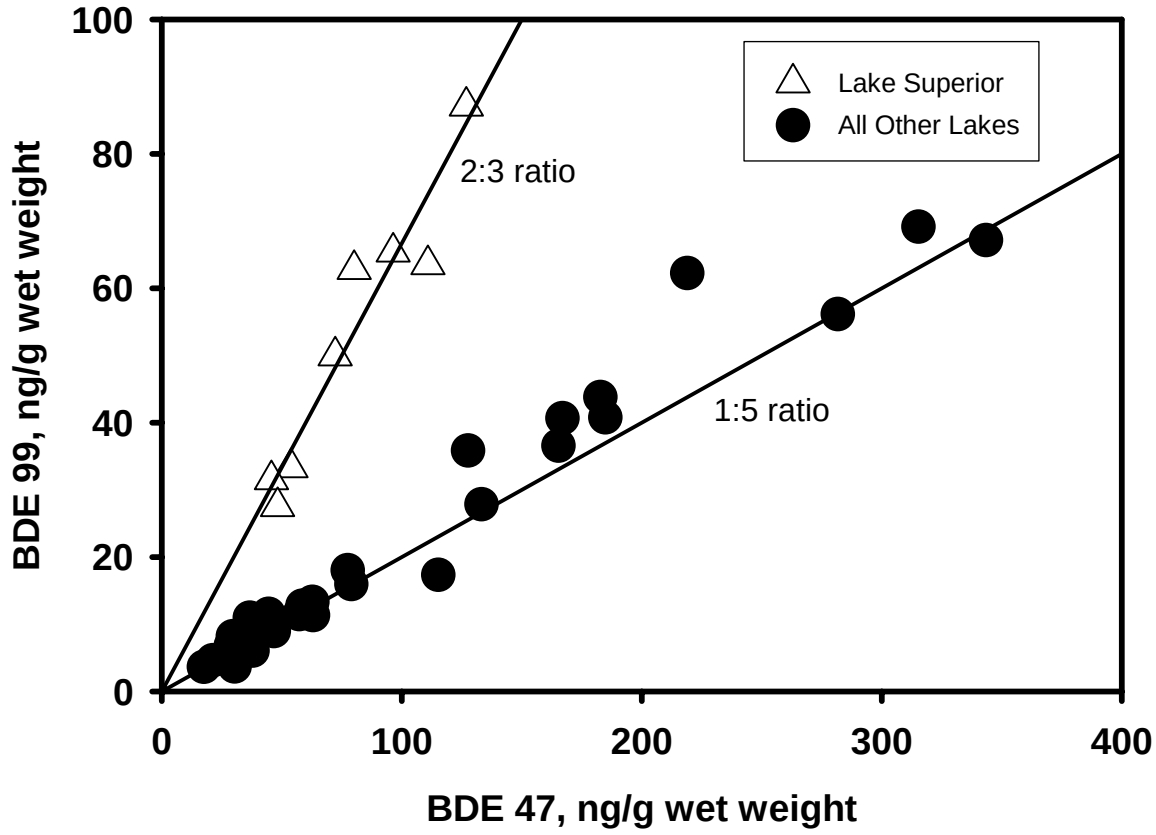
100
80
60
40
20
0
0
100
200
300
400
BDE 99, ng/g wet weight
BDE 47, ng/g wet weight
Lake Superior
All Other Lakes
2:3 ratio
1:5 ratio

FIG 9